Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.201200166

Development and Performance of Boron Carbide-Based Smoke Compositions

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Abstract: Pyrotechnic smoke compositions for visual obscuration containing boron carbide, potassium nitrate, potassium chloride, and various lubricants are described. Only the waxy lubricants stearic acid and calcium stearate slowed the burning rate into a range suitable for end-burning smoke grenades. For compositions pressed into steel cans, the addition of just 2 wt-% calcium stearate was shown to reduce the burning rate from 0.50 $cm\,s^{-1}$ to 0.09 $cm\,s^{-1}$. In this system, potassium chloride serves as a diluent that reduces incandesence but also increases slag formation. Compositions containing potassium chloride in the 25–30 wt-% range exhibited both acceptably low incandescense and slag formation upon burning, while also producing copious amounts of white smoke. These experimental compositions were loaded into full-size grenade cans; field and smoke chamber testing revealed that they outperform the US Army's in-service M83 TA grenade both qualitatively and quantitatively. The photopic mass-based figures of merit for experimental grenades KCl-25, KCl-30, and a production-run M83 TA grenade were 2.51, 2.19, and 1.44 $m^2\,g^{-1}$, respectively.

Keywords: Pyrotechnics · Smoke · Boron carbide · Environmental

1 Introduction

Pyrotechnic smoke compositions are used for signaling, for marking targets, and for screening troop movements. For many years, hexachloroethane (HC) smoke compositions were widely used by the US Army as high-performance visual obscurants. These munitions are no longer manufactured for US Army use because of the toxicity of hexachloroethane [1] and the resulting $ZnCl_2$-based smoke [2,3]. Red phosphorus (RP) compositions have been considered as replacements but they are notoriously sensitive [4] and have stability issues [5]. Terephthalic acid (TA) smoke compositions were originally developed for use in less-toxic training grenades. In this capacity, the lower obscuration performance of the TA smoke was not problematic. However, with HC grenades no longer readily available, soldiers must now use the TA smoke grenade in combat, with unsatisfactory results. Matching HC's visual obscuration performance is no longer a hard-and-fast requirement for a new tactical smoke grenade. Instead, in recognition of the performance/toxicity trade-off, there is now a need for compositions of acceptable toxicity that offer performance greater than the currently used TA smokes.

Recent research towards the development of a less toxic "HC substitute" smoke composition has involved the pyrotechnic dissemination of benign salts and oxides. Webb has developed cellulose/Mg/$NaClO_3$/$CaCO_3$ compositions which produce smoke intended to mimic aerosolized sea salt [6]. Blau has reported compositions based upon the B/KNO_3 system diluted with various alkali chlorides [7]. A similar approach was examined earlier by Krone in the 1980s. In that work, the Mg/KNO_3 fuel/oxidizer pair was diluted with KCl and other salts [8,9]. Provided the energy of these systems remains high enough, both the diluent salts and the combustion products of the fuel/oxidizer pair are volatilized and recondense to give smoke.

Boron carbide was recognized as a pyrotechnic fuel many years ago, but it has since been overlooked. A 1961 patent describes several smoke compositions containing B_4C, $KMnO_4$, and other oxidizers [10]. Binary B_4C/oxidizer mixtures were evaluated as smoke compositions by Lane and co-workers and described in 1968 [11,12]. More recently, the B_4C/KNO_3 system has been demonstrated as a green illuminant, and holds promise as an environmentally benign replacement for barium chloride-based compositions [13]. Inspired by these reports, especially by the more recent illumination work, we have examined the B_4C/KNO_3 system as the basis for smoke compositions that contain additional salt diluents (like the systems described in the previous paragraph) and other additives to control burning rate [14]. The choice of a nitrate oxidizer, KNO_3, was also

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
06 MAR 2013	**N/A**	**-**

4. TITLE AND SUBTITLE
Development and Performance of Boron Carbide-Based Smoke Compositions

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Anthony P. Shaw, Jay C. Poret, Robert A. Gilbert, Jr., Joseph A. Domanico, Ernest L. Black

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Armament Research, Development and Engineering Center, US Army RDECOM-ARDEC, Picatinny Arsenal, NJ 07806, USA

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR’S ACRONYM(S)

11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Pyrotechnic smoke compositions for visual obscuration containing boron carbide, potassium nitrate, potassium chloride, and various lubricants are described. Only the waxy lubricants stearic acid and calcium stearate slowed the burning rate into a range suitable for end-burning smoke grenades. For compositions pressed into steel cans, the addition of just 2 wt% calcium stearate was shown to reduce the burning rate from 0.50 cm/s to 0.09 cm/s. In this system, potassium chloride serves as a diluent that reduces incandesence but also increases slag formation. Compositions containing potassium chloride in the 25-30 wt% range exhibited both acceptably low incandescense and slag formation upon burning, while also producing copious amounts of white smoke. These experimental compositions were loaded into full-size grenade cans; field and smoke chamber testing revealed that they outperform the US Armys in-service M83 TA grenade both qualitatively and quantitatively. The photopic mass-based figures of merit for experimental grenades KCl-25, KCl-30, and a production-run M83 TA grenade were 2.51, 2.19, and 1.44 m2/g, respectively.

15. SUBJECT TERMS
pyrotechnics, smoke, boron carbide, environmental

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**7**	

motivated by increasing environmental regulation targeting perchlorates [15].

In any pyrotechnic smoke composition, two important qualities are control of burning rate and low slag production upon burning. The former allows adaptability to different burning time requirements. The latter allows the use of simple and compact end-to-end burning designs without the risk of clogging or case rupture. Our preliminary work indicated that the B_4C/KNO_3 pair, when combined with KCl as a diluent and calcium stearate as a burning rate modifier, could display these desirable characteristics. A composition containing 13 wt-% B_4C, 60 wt-% KNO_3, 25 wt-% KCl, and 2 wt-% calcium stearate was identified as a promising candidate in preliminary small-scale experiments. Here, we report detailed studies focused on burning rate and slag formation, as well as the results of large-scale field and smoke chamber tests.

2 Experimental Section

2.1 Material Properties and Composition Mixing

Potassium nitrate (MIL-P-156B) and stearic acid (19-5010) were obtained from Hummel Croton. Graphite (282863) and polytetrafluoroethylene (430943) were obtained from Sigma Aldrich. Boron carbide (43002), calcium stearate monohydrate (39423), hexagonal boron nitride (11078), and granular potassium chloride (11595) were obtained from Alfa Aesar. The potassium chloride was ball milled until it passed through a 50 mesh (300 μm) screen. For the powdered chemicals, a Malvern Morphologi G3S optical microscopy particle size analyzer was used to determine number-based CE diameter distributions; volume-based distributions were calculated (Table 1). The smoke compositions are dry mixtures of three or four components. They were prepared by a combination of tumbling and screening (30 mesh, 590 μm) steps.

2.2 Test and Analysis Protocols

Small cylindrical pellets (1 g, 0.95 cm diameter) were prepared by pressing compositions in a die at 69 MPa. These pellets were used for the slag study. The test container consisted of an insulating ceramic fiber disk placed inside a steel cup (1.27 cm tall, 2.22 cm diameter). Each pellet was placed on the insulating disk in this cup and then ignited with an electrically heated nichrome wire. The slag, as a percentage of original pellet mass, was determined by weighing the cups before and after combustion. For each composition, five pellets were tested and the results were averaged.

Compositions pressed into stainless steel cups were used for burning rate studies. The cups, cylindrical and closed on one end, had a 1.75 cm inner diameter, 4.0 cm height, and a 1.0 mm wall thickness. The compositions (13–14 g) were pressed at 69 MPa. An igniter slurry composed of 33.0 wt-% potassium nitrate, 24.5 wt-% silicon, 20.8 wt-% black iron oxide, 12.3 wt-% aluminum, 3.8 wt-% charcoal, and 5.6 wt-% nitrocellulose in acetone was applied. These items were dried overnight in a 65 °C oven. The mass of dried igniter composition on each cup was approximately 1 g. An electrically heated nichrome wire was used for ignition. Digital video recordings were used to determine burning times. The lengths of the compositions were divided by the burning times to obtain average linear burning rates. For each composition, three cups were tested and the results were averaged.

Full-size experimental grenades were made for field and chamber tests. Both end-burning (analogous to the M8 HC grenade) and core-burning (analogous to the M83 TA grenade) versions were prepared. Unlike the M83, the experi-

Table 1. Particle size data/μm.

Material (Formula)	CE Diam.[a] (D[4,3])[b]	D[n, 0.1][c] (D[v, 0.1])[d]	D[n, 0.5][c] (D[v, 0.5])[d]	D[n, 0.9][c] (D[v, 0.9])[d]
boron carbide	3.48	0.59	1.64	9.05
(B_4C)	(19.97)	(7.89)	(15.24)	(29.37)
potassium nitrate	7.31	2.02	5.80	13.98
(KNO_3)	(31.88)	(10.28)	(26.19)	(59.13)
calcium stearate	5.83	1.82	4.57	10.81
($C_{36}H_{70}O_4Ca \cdot H_2O$)	(22.23)	(7.84)	(19.54)	(36.60)
graphite (C)	5.53	2.03	4.57	10.19
	(15.81)	(6.22)	(11.96)	(22.99)
PTFE $(C_2F_4)_x$	9.92	2.91	8.21	18.61
	(30.07)	(11.87)	(27.86)	(49.72)
boron nitride	6.39	2.18	5.53	11.42
(hexagonal, BN)	(21.79)	(7.16)	(14.16)	(42.68)
stearic acid	11.50	2.40	5.91	25.51
($C_{18}H_{36}O_2$)	(90.01)	(29.36)	(83.92)	(154.50)

a) Number-based CE (circle-equivalent) mean diameter. b) Volume mean diameter. c) D[n, *x*] is the diameter at which (100·*x*)% of the number distribution is below. d) D[v, *x*] is the diameter at which (100·*x*)% of the volume distribution is below.

mental core-burning grenades were configured to vent smoke from both ends of the can. Each experimental grenade contained 350 g of smoke composition. Weather conditions for the field tests were 37 °C and 50 % relative humidity with an 8 km h^{-1} wind. An M83 TA grenade (PBA manufacture) was tested along with the experimental grenades for comparison. For the end-burning grenades, average linear burning rates were calculated by dividing the composition lengths by the burning times.

Obscuration measurements were performed in the Edgewood Chemical Biological Center's 190 m^3 smoke chamber. The end-burning experimental grenades were used for these measurements and were tested at 23.9 °C and 50 % relative humidity. After each grenade was functioned and the smoke was equilibrated with a mixing fan, the aerosol concentration was determined gravimetrically by passing a known volume through a filter disk. The calculated total mass of aerosol was divided by the initial mass of smoke composition to give the yield factor. An Ocean Optics DH2000 deuterium tungsten halogen light source and HR2000 UV/Vis spectrometer were used to determine transmittance as a function of wavelength in the visible spectrum across a 6 m path length. Smoke was vented from the chamber until the transmittance was about 0.2, at which point it was recorded and the aerosol concentration was redetermined. These data were used to calculate the extinction coefficient as a function of wavelength in the visible spectrum. Figures of merit were then calculated (see Section 3.3). Photopic values were calculated by using transmittance as a function of wavelength that was weighted to the photopic response of the human eye [16].

3 Results and Discussion

3.1 Effect of Lubricants on Burning Rate

$B_4C/KNO_3/KCl$ compositions that contain no additives burn too rapidly for use in smoke grenades, regardless of the ratio of these components. Certain organic compounds, such as melamine, are known to retard burning rate in propellants [17] and illumination flares [18]. However, melamine and several other organics have essentially no influence on burning rate in this system. In contrast, the waxy organic lubricants calcium stearate and stearic acid were found to have a strong influence, slowing burning rate dramatically. A similar influence has also been found in the gassy $W/Sb_2O_3/KIO_4$ pyrotechnic delay, where calcium stearate was used to obtain slow burning rates [19].

Lubricants generally improve consolidation and reduce void space in pressed compositions. In gassy pyrotechnics, this hinders the flow of hot combustion gases within the pellet to unburnt layers, thereby slowing the burning rate [20]. However, this effect cannot be considered in isolation. The individual chemical and physical properties of lubricants are also quite important. To gain a better understanding, three other lubricants were tested alongside calcium stearate and stearic acid at the 2 wt-% level (Table 2). While all the lubricants aided consolidation and reduced void space (as indicated by %TMD, the density as a percentage of theoretical maximum), only calcium stearate and stearic acid slowed the burning rate.

Table 2. Effect of lubricants[a].

Lubricant	Consolidated Density/g cm^{-3}	%TMD[b]	Burning Rate/cm s^{-1}
none[c]	1.70	80.3	0.50
BN (hex)	1.75	82.5	0.49
graphite	1.76	82.9	0.51
PTFE	1.78	83.7	0.47
stearic acid	1.77	85.7	0.06
calcium stearate	1.80	86.7	0.09

a) Stainless steel cups containing 13/60/25/2 mixtures of B_4C/KNO_3/KCl/lubricant consolidated at 69 MPa. b) Consolidated density as a percentage of theoretical maximum. c) Data for a 13/62/25 $B_4C/KNO_3/KCl$ composition.

Stearates are distinguished by their low melting points. Calcium stearate monohydrate (the type used in this study) dehydrates at 100–110 °C, begins to soften at 125 °C, and is molten by 160 °C [21,22]. Stearic acid melts at an even lower temperature, 69 °C [23]. These melting events are endothermic. As low energy fuels, stearates effectively serve as diluents (their decomposition-oxidation is less energetic than the oxidation of high energy fuels such as Mg or B_4C). Stearates are also thermal insulators that inhibit heat flow within a pyrotechnic grain. As a result of these characteristics, stearates can slow burning rates even in situations where there is effectively no void space, such as in hot-molded Mg/PTFE based pyrolants [24,25]. In compositions that are not as well consolidated, void space is an important factor and the excellent lubricating properties of stearates lead to high %TMD values, as demonstrated in Table 2. Thus, the profound influence of these lubricants on burning rate in the subject smoke compositions appears to be caused by multiple coinciding and reinforcing factors involving thermodynamics, thermal conductivity, and consolidation, as described above.

In contrast, the other lubricants in Table 2 have some physical and chemical properties that are not conducive to slowing burning rate. Hexagonal boron nitride has an extremely high melting point (2600 °C) [26] while graphite does not melt at atmospheric pressure [23]. These materials serve as diluents, but they are reasonably good thermal conductors [25,26] and can also transmit heat by the absorption and re-emission of infrared radiation. PTFE is a thermal insulator that melts at a fairly low temperature, 333 °C [27], but it is also a potent pyrotechnic oxidizer and its participation in this role cannot be precluded. Additionally, the boron nitride, graphite, and PTFE compositions were not consolidated as effectively as those containing calcium stearate or stearic acid, as indicated by their lower %TMD values.

While the compositions containing stearic acid generally burn more slowly than those containing calcium stearate, the former exhibit undesirable flaming. Calcium stearate was therefore chosen for more detailed studies. As calcium stearate was added to a stock 13/62/25 mixture of B_4C/KNO_3/KCl, both consolidated density and %TMD increased (Figure 1) while burning rate decreased (Figure 2). The effect was greatest in the 0–1 wt-% range. From 1–5 wt-%, the change in %TMD was greater than the change in consolidated density (calcium stearate is less dense than the base composition).

Burning rates between 0.05 and 0.20 cm s^{-1} are desirable for end-burning smoke grenades. In a typical grenade, these rates would correspond to a burning time of 45–180 s. The calcium stearate level may be used to tune burning rate within this range at a *constant* loading pressure. As is the case with other gassy pyrotechnic systems [20], loading pressure also affects burning rate (see Section 3.3), but not enough to serve as the primary method for burning rate control.

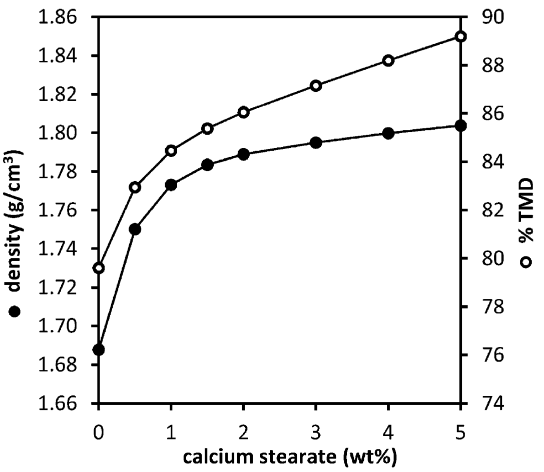

Figure 1. Effect of calcium stearate level on consolidated density (closed circles) and calculated %TMD (open circles). Compositions were prepared from a stock 13/62/25 mixture of B_4C/KNO_3/KCl and added calcium stearate. Compositions were pressed in stainless steel cups at 69 MPa.

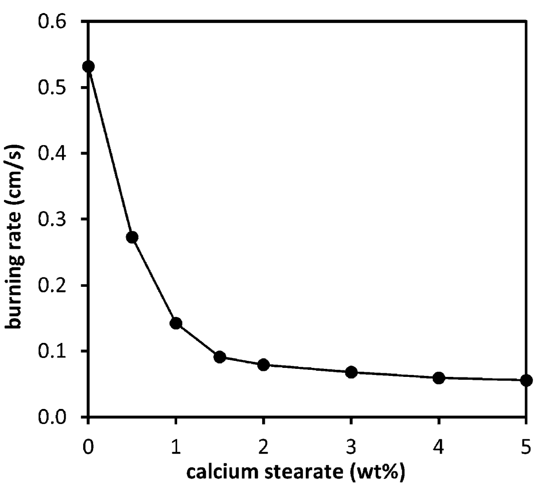

Figure 2. Burning rate as a function of calcium stearate level for the compositions in Figure 1.

3.2 Effect of Varying KCl Content

Blau [7] and Krone [8, 9] used the dilutive properties of salts such as KCl in the development of their smoke compositions. The addition of such diluents to energetic fuel/oxidizer pairs serves to reduce incandescense and can mark the distinction between a smoke composition and an illuminant. The subject B_4C/KNO_3/KCl smoke compositions provide a good example – as previously mentioned, the same system without added KCl is the basis of recently reported green illuminants [13].

In addition to supressing light output, added KCl results in an increased amount of slag produced upon combustion. This is deleterious to smoke performance, as the slag consists of condensed phase products that were not volatilized and subsequently recondensed as an aerosol. Figure 3 shows the increase in slag produced as the KCl level is varied in the 20–50 wt-% range. Compositions containing 25–30 wt-% KCl provided the proper balance between light output and slag production upon burning, and produced copious amounts of white smoke. They were therefore selected for experiments in full-size grenade hardware.

3.3 Field Tests and Chamber Measurements

Both end-burning and core-burning experimental grenades were prepared. Despite the lower consolidated densities and %TMD values in comparison to earlier experiments, reasonably slow burning rates were still achieved (Table 3).

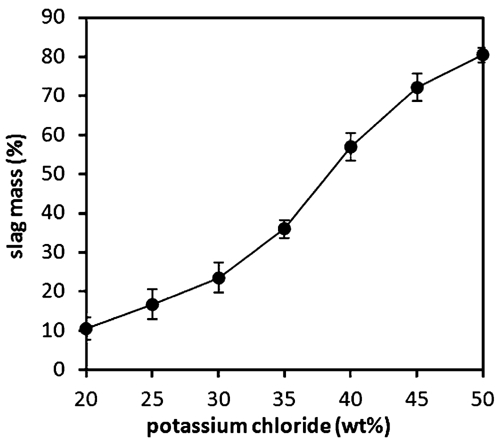

Figure 3. Effect of varying KCl content on experimental slag percentage. For 13/(85−*x*)/*x*/2 mixtures of B_4C/KNO_3/KCl/calcium stearate pressed as bare pellets at 69 MPa. The error bars show two standard deviations.

Table 3. Smoke grenade results.

Grenade[a)]	Consolidated Density/g cm^{-3}	%TMD	Burning Rate/cm s^{-1} [b)]	Burning Time/s
KCl-25 (end)	1.52	73.1	0.130	65
KCl-25 (core)	1.57	75.5	–	22
KCl-30 (end)	1.52	73.4	0.134	63
KCl-30 (core)	1.59	76.7	–	21
M83[c)]	–	–	–	62

a) KCl-25 contained 13 wt-% B_4C, 60 wt-% KNO_3, 25 wt-% KCl, and 2 wt-% calcium stearate. KCl-30 contained 13 wt-% B_4C, 55 wt-% KNO_3, 30 wt-% KCl, and 2 wt-% calcium stearate. End-burning and core-burning grenades were consolidated at 24.5 and 25.6 MPa, respectively. b) Only calculated for the end-burning grenades. c) M83 TA grenade (PBA manufacture).

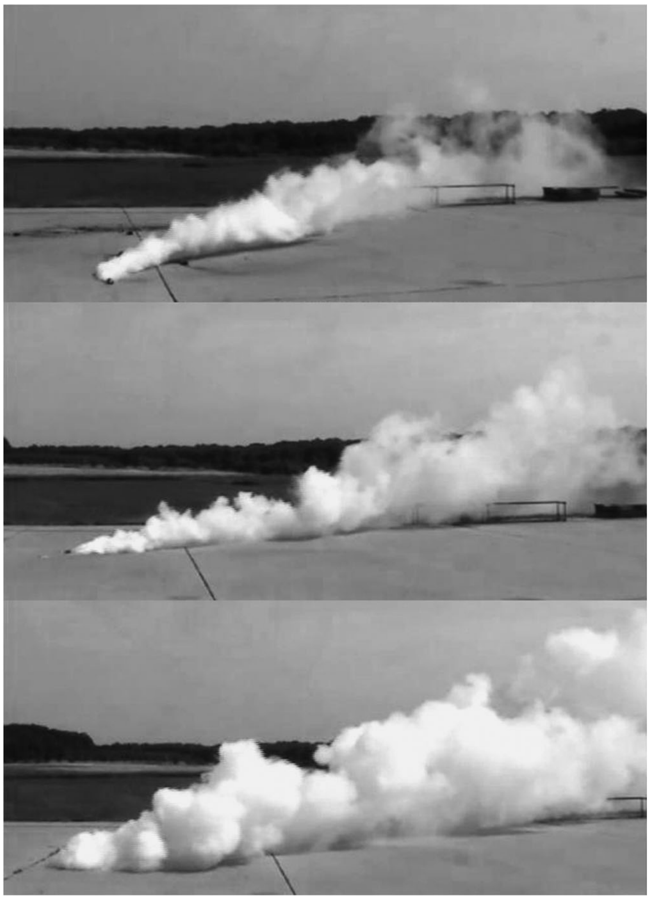

Figure 4. Field tests of full-size smoke grenades. M83 TA (PBA manufacture) (top); KCl-25 end-burning (middle); KCl-25 core-burning (bottom).

In the end-burning configuration, the experimental grenades burned for over a minute, slightly exceeding the burning time of an M83 TA smoke grenade. The core-burning experimental grenades, which burned from the top down and from the center core outward, produced the same quantity of smoke in one third of the time (Figure 4). Qualitatively, the KCl-25 grenades were better than the KCl-30 variants and all of the experimental grenades were better than the M83 TA grenade. The experimental smoke clouds were notable for their persistence, maintaining thickness as they moved across the test field. In contrast, the M83 TA smoke cloud thinned rapidly.

End-burning experimental grenades were used for obscuration measurements (Table 4). Figures of merit (FM) were determined by using an equation based on the Beer–Lambert law [28]:

$$\mathrm{FM} = \alpha \cdot Y = \left(\frac{-V \cdot \ln(T)}{m_\mathrm{a} L}\right)\left(\frac{m_\mathrm{a}}{m_\mathrm{c}}\right) = \frac{-V \cdot \ln(T)}{m_\mathrm{c} L}$$

As none of the smokes had any distinct spectral features in the visible spectrum, the photopic extinction coefficients (α) and figures of merit were not significantly different from the corresponding values at 555 nm, the wavelength of peak photopic response [16]. While the extinction coefficients for KCl-25 and KCl-30 were lower than those for the M83, the experimental grenades had significantly higher yield factors (Y). This resulted in their greater performance as indicated by their higher figures of merit. The quantitative ranking KCl-25 > KCl-30 > M83 as indicated by Table 4 is in agreement with qualitative observations from the field tests.

4 Conclusion

A variable burning rate, high aerosolization efficiency, and high obscuration performance are all desirable qualities in a pyrotechnic smoke composition. Four-component mix-

Table 4. Smoke chamber results.

Grenade	Y [a)]	α/m^2 g^{-1} [b)] 555 nm	α/m^2 g^{-1} [b)] Photopic[d)]	FM/m^2 g^{-1} [c)] 555 nm	FM/m^2 g^{-1} [c)] Photopic[d)]
KCl-25[e)]	0.70	3.63	3.59	2.54	2.51
KCl-30[e)]	0.60	3.73	3.68	2.22	2.19
M83[f)]	0.30	4.85	4.80	1.46	1.44

a) Yield factor. b) Mass extinction coefficient. c) Figure of merit. d) Determined by weighting transmittance to the photopic response of the human eye. e) Experimental end-burning grenades tested at 23.9 °C and 50% relative humidity. f) M83 TA grenade (PBA manufacture) tested at 21.7 °C and 61% relative humidity.

tures of B_4C, KNO_3, KCl, and calcium stearate appear to have these qualities. They are promising candidates for use in smoke munitions where improved performance over currently used TA compositions is desired. They are currently under consideration for use in a variety of smoke munitions in addition to smoke grenades. Continuing and future research in our laboratories includes chemical characterization of the smoke, determining the effects of varying temperature and humidity, and thorough toxicological evaluations. These studies will be the subjects of forthcoming reports.

Symbols and Abbreviations

HC	hexachloroethane
RP	red phosphorus
TA	terephthalic acid
PTFE	polytetrafluoroethylene
wt-%	weight percent
µm	micrometer
nm	nanometer
MPa	megapascal
%TMD	density as % of theoretical maximum
PBA	Pine Bluff Arsenal
FM	figure of merit/$m^2\,g^{-1}$
Y	yield factor, (m_a/m_c) unitless
α	mass extinction coefficient/$m^2\,g^{-1}$
m_a	mass of aerosol/g
m_c	mass of starting smoke composition/g
V	volume of chamber/m^3
L	path length/m
T	transmittance/unitless

Acknowledgments

The authors thank *Christopher M. Csernica* for the use of his laboratory space and *Karl D. Oyler* for performing particle size measurements. *Lawrence A. Bickford*, *Gary Chen*, and *Russell N. Broad* are thanked for useful discussions. The US Army is thanked for funding this joint ARDEC-ECBC project through the RDECOM Environmental Quality Technology (EQT) Program.

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Received: October 5, 2012
Revised: November 26, 2012
Published online: March 6, 2013